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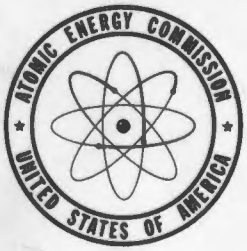

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ZIRCONIUM IONS IN AQUEOUS SOLUTION*

by Edgar Harrison Dewell and Adolf F. Voigt

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Iowa State College

I. ABSTRACT

The ion exchange properties of zirconyl chloride have been studied in solutions 1.4 x 10^{-3} M in zirconium and .52 M in ammonium chloride; the cationic content of the solutions was found to vary from 99 per cent to about 55 per cent as upper limits in the acid range 1.62 x 10^{-2} M to 3.55 x 10^{-3} M.

A time dependency of the exchange of zirconium was noted and in an attempt to discover its nature conductance measurements at 10^{-4} M zirconium were made as time studies. Conductance curves were run at 25° and 35° C.; unfortunately they were not subject to analysis in terms of the probable species present. At least three conducting species were present in the solutions and the measurements permitted the simultaneous observation of only two. The measurements are believed to be among the most accurate so far reported and the concentrations investigated were much below the previous reports.

Further studies along the lines of this investigation have been outlined for obtaining additional information on the aqueous behavior of zirconyl chloride.

II. INTRODUCTION

The commerical possibilities of zirconium and its occurrence as a fission product in the nuclear reactor have created a demand for a more intimate understanding of the composition of its aqueous solutions. Much of the work that has been done on zirconium solutions is purely

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* From an M.S. thesis by E. H. Dewell, submitted June, 1951.

descriptive although its solid compounds have been quite extensively studied.

Zirconium is a metallic element, highly reactive, and apparently uniformly quadrivalent in solution. Trivalent and divalent zirconium have been reported in vapor phase reactions but these are outside the domain of this discussion. Zirconium compounds are strongly hydrolyzed and cannot be recovered from solution as neutral salts; instead, basic salts representing some degree of hydrolysis are obtained. Zirconium readily forms complexes with a number of ions and molecules and its solutions are thereby rendered remarkably stable. It is the purpose of this investigation to add to the meagre information on the hydrolysis of zirconyl chloride in very dilute solutions.

III. HISTORICAL BACKGROUND

When zirconium tetrachloride is dissolved in water, it undergoes an immediate hydrolysis and the solution becomes highly acid. If such a solution is evaporated to super-saturation and allowed to crystallize, a solid material, known as zirconyl chloride, corresponding to the empirical formula $ZrOCl_2 \cdot 8H_2O$ is recovered. Apparently the crystal structure of this body has never been fully investigated and its true nature is unknown. The fact that it is so readily prepared from aqueous solutions has lead many investigators to conclude that it is a true compound and ionizes according to the following reaction:

$$ZrOCl_2 \rightleftharpoons ZrO^{++} + 2Cl^-,$$

and that the purported ZrO^{++} ion is the main species in its aqueous solutions over very large concentration ranges. In an attempt to verify its existance Chauvenet[1] performed a conductometric titration of a aqueous solution of zirconium tetrachloride with sodium hydroxide and announced an inflection in his titration curve at the equivalence point for the formation of the zirconyl ion. Some years later Britton,[2] investigating such solutions potentiometrically, concluded that even when quite dilute zirconium tetrachloride, though considerably hydrolyzed, makes an appreciable contribution to the system; the zirconyl ion as a unique entity appeared to be an artifact.

Other investigators have attacked the problem by differing methods with the same end in view. As early as 1905 Ruer[3] discovered that the conductivity of zirconyl chloride changes with time, showing the hydrolysis to be a highly complicated reaction. In 1920 Venable and Jackson repeated Ruer's work[4] and observed that the rate of change of conductivity was dependent on both the temperature and concentration of zirconium. Their data are presented as Figure 1. It will be observed that they abandoned their measurements after a few hours, presumably because of inadequate temperature control. Indeed they stated that solutions of zirconyl chloride reach their maximum hydrolysis in approximately three hours. This was shown to be erroneous by Pauli and Adolf[5] and again by the present investigation. None of the conductivity data has been explained on the basis of any specific zirconium species. Pauli and Adolf[5] extended the work on zirconium solutions and carried out an exhaustive study of the properties of aged zirconyl chloride solutions in the concentration range 2.2×10^{-3} to 0.25 M. They measured the conductivity, determined the pH, investigated the freezing points, and observed the ion migration under an impressed field. They noted that zirconium migrates to both the anode and cathode. They logically concluded that simple ionization of zirconyl chloride in aqueous solutions was unimportant and that its properties were governed by hydrolysis and complex ion formation. They postulated the existence of a variety of polymeric ions. Although their work was quite carefully done the assumptions they made are now open to question, e.g. they discounted the possibility of $Zr(OH)_3^+$ existing as a hydrolysis product and eliminated it from their discussion. Further work in this direction was not reported until 1940 when Laubengayer and Eaton[6] attempted to determine the extent of hydrolysis of zirconyl chloride by measuring its acidity at various dilutions in .1 M KCl using a glass electrode. They arrived at the tentative conclusion that an average of three hydroxyl ions is associated with each zirconium over the concentration range 10^{-2} to 10^{-4} M. This conclusion was based on the assumption that all the zirconium in the solutions was present as ionic species and that none was colloidal. In an ion exchange study Ayres[7] showed that at a concentration of 3.8×10^{-2} M zirconyl nitrate does not exchange with a resin, indicating the presence of colloidal or anionic forms. Complexing of zirconium by nitrate and chloride has been investigated[8] and is reported to be of negligible magnitude; one would therefore expect similar hydrolytic behavior of the two. The possible existence of colloidal forms in the

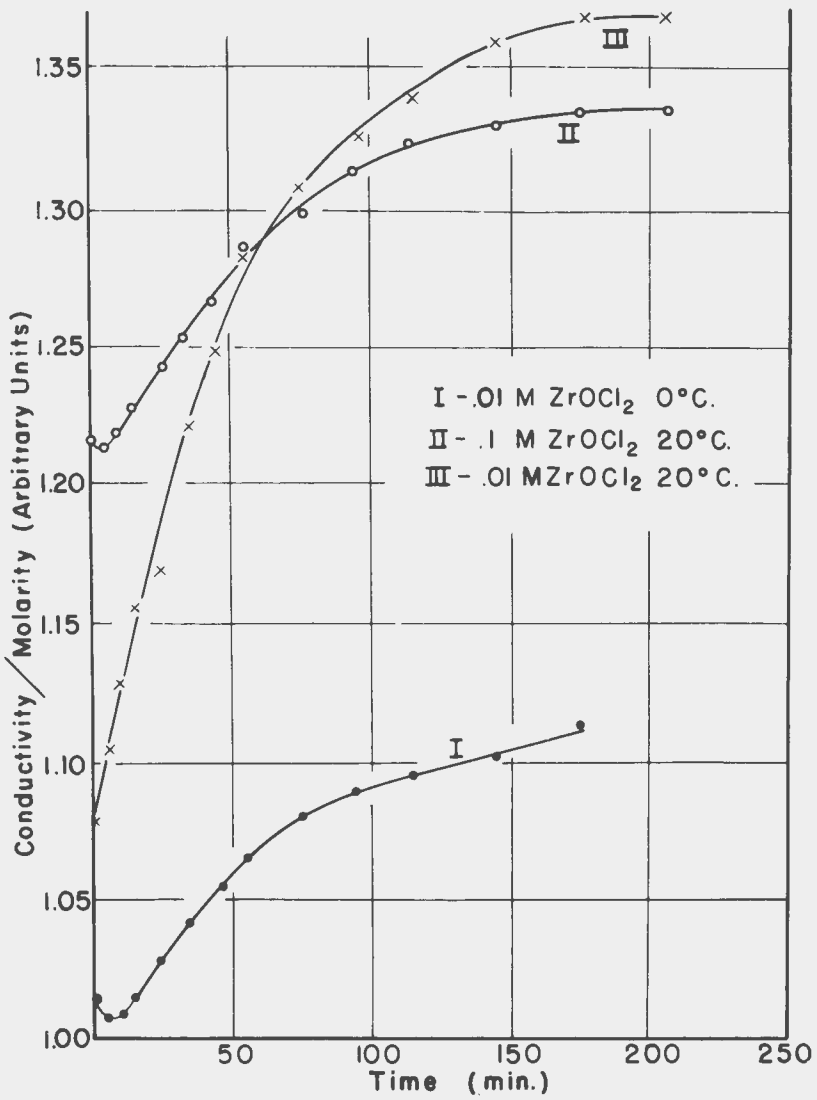


Fig. 1 Conductivity of $ZrOCl_2$ with Time
(Plotted from data of Venable and Jackson)

chloride must therefore be admitted and the conclusions on hydrolysis measured by pH determination modified accordingly.

Perhaps the most detailed investigation to date on the composition of zirconium solutions was reported by Connick and McVey[8] in 1949. They made up dilute solutions of zirconyl chloride in 2.00 M perchloric acid and shook the solutions with a benzene solution of thenoyl trifluoroacetone, a complexing agent for tetravalent zirconium which extracts the zirconium into the benzene phase as an uncharged molecular chelate in equilibrium with the ionic forms of zirconium in the aqueous phase. They investigated the very dilute range -- from the carrier free activity supplied by the Atomic Energy Commission to 10^{-3} molar. Their work in 2 M perchloric acid shows that the ion $ZrOH^{+3}$ predominates and that polymerization effects are negligible. Extending the method of Connick and McVey,[8] Connick and Reas[9] investigated the polymerization of zirconium in 1.00 and 2.00 M perchloric acid. They found that at very low zirconium concentrations unhydrolyzed Zr^{+4} ion was the predominating species but that polymers began to appear in 1.00 M perchloric acid at 2×10^{-4} M and in 2.00 M acid at 2×10^{-3} M.

In view of the results obtained by Ayres[7] it appears that a study of the ion-exchange equilibria of zirconium solutions versus acid concentration in the very dilute range should supply considerable information on the relative amounts of zirconium existing as colloidal or ionic species, bearing in mind that the existence of colloidal matter was generally ignored in the observations just reviewed. Accordingly, a series of experiments with Nalcite HCR was run using a tracer method of analysis at a zirconium concentration of 10^{-3} molar.

The exchange data show a time dependency. In an attempt to discover the nature of the slow reaction the conductivity of zirconyl chloride was investigated as a function of time. The concentration used was 10^{-4} molar, much below those previously reported. The hydrogen ion concentration was measured at the initial and final points taken. The two sets of experiments are reported as parts one and two.

IV. PART I. ION EXCHANGE STUDY

A. General Method

Samples of exchange resin oven-dried at 95° C. were equilibrated with zirconyl chloride solutions of varying pH at 25.00 ± 0.05° C. for a period of about eight hours. The zirconium was innoculated with Zr^{95} as a tracer, and the concentration of zirconium was determined after equilibration by differential counting of an aliquot of the solution.

B. Preparation of Materials

1. Exchange Resin

Forty to sixty mesh Nalcite HCR* was used in this study. It is a sulfonic acid type exchanger of very high capacity and only one type of exchanging group. It is supplied by the manufacturer as small spheres in the sodium form. The resin was backwashed and then conditioned by passing it from the sodium to the hydrogen forms with hydrochloric acid, from the hydrogen to the ammonium cycle with ammonium chloride, from the ammonium back to the sodium cycle with sodium chloride, and finally back to the hydrogen cycle with hydrochloric acid. Five per cent feed solutions were used in all cases. Flame tests for sodium and pHydrion test paper were used to monitor the cycle changes. Backwashing and conditioning are necessary for all exchange resins in order to remove fines and dust as well as foreign ions picked up in manufacture.

Nalcite is extremely hygroscopic and offered some difficulty in obtaining reproducible weights. Air dried samples of approximately 250 mg. were placed into small screw-topped bottles and were dehydrated at 95° C. The bottles were left open in the oven and were capped on removal while still hot; the bottles were then dipped in fifty percent ethanol-water to cool the sample rapidly and saturate the glass with water. Each vial was wiped dry with absorbent tissue, the top loosened momentarily to equalize pressures, and weighed immediately. About three days at 95° was required for the dehydration. The dried samples were observed to gain weight in a very few

*Nalcite HCR, marketed by the National Aluminate Corp., Chicago, Ill., is indentical with Dowex-50 manufactured by the Dow Chemical Co.

minutes even though tightly stoppered; all weights were therefore taken within one minute after removal from the oven. Nalcite kept in glass picks up very large static charges if it is shaken, and though the static charge apparently did not affect the weights of the samples -- tested by charging a sample by severe shaking -- it complicated the handling of the dry resin. Dry Nalcite defies attempts at quantitative transfer between glass containers and two samples were lost on one very dry day because the repulsion between particles was sufficient to cause them to pop over the sides of a 150 ml. Pyrex beaker. Samples were therefore handled with as little friction as possible, and sample weights were obtained by difference in vial weights after quickly dumping the vials into 250 ml. beakers. Any moisture picked up by the resin remaining inside the vial while it was uncapped was ignored.

The replaceable hydrogen content of the resin was measured by a potentiometric titration of the resin with standard sodium hydroxide. The titration curves (see Figure 2) are characteristic of strong acids with only one equivalence point. The sodium hydroxide was added in the presence of the resin which was stirred magnetically. Because this type of resin has only one active group, i.e. sulfonic acid, no variation in resin capacity with pH should be expected. The value obtained for the available hydrogen by this titration was assumed to apply throughout the pH range. Since a number of resins[10] do not behave in this manner, this particular resin was chosen for this investigation.

2. Zirconyl Chloride

Hafnium-free ($< 0.5\%$) zirconyl chloride was obtained from Dr. R. S. Hansen of this laboratory. The sample contained a trace of iron which was removed by a number of recrystallizations of the material from concentrated hydrochloric acid until no further test for iron was observed.

3. Zirconium Tracer

Carrier-free Zr^{95} in equilibrium with its Nb^{95} daughter activity was obtained as an oxalate complex in 5% oxalic acid from the Oak Ridge National Laboratory.

Schubert and Conn[11] have indicated that equilibration of tracer and carrier zirconium may be difficult due to the radio-colloidal behavior of the active solutions; precaution must be taken to make certain that the solutions are in equilibrium. Any inhomogeneity in specific activity wil

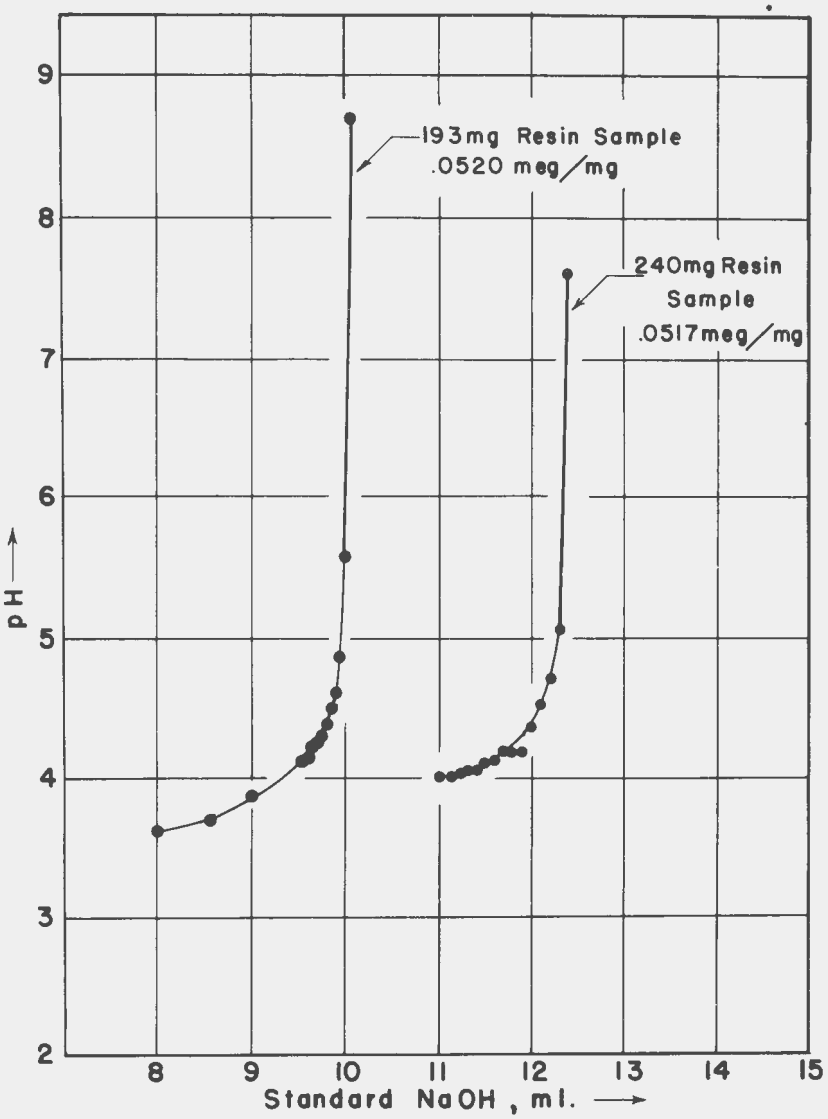


Fig. 2 Potentiometric Titration Nalcite HCR

produce large errors in concentrations calculated on the basis of radiation assay of samples. They showed that radio-colloidal formation is greatly diminished at high acid concentrations. Toward that end an apparatus was built for refluxing the carrier with the tracer and concentrated hydrochloric acid. It was designed for refluxing a ten milliliter sample and is shown as Figure 3.

A sample of the active solution equivalent to about 10^7 counts per minute was placed in the reflux condenser together with a 1.00 ml. sample of 1.14 M zirconyl chloride (standardized gravimetrically). It was refluxed with 5 ml. of 12 M HCl and 1 ml. of 30% hydrogen peroxide for twenty four hours. Thus in one operation the oxalic acid present in the tracer solution was removed by oxidation, and the activity was equilibrated with the carrier. Small amounts of peroxide were added at intervals during the refluxing. At the end of the process the solution gave negative results when tested for oxalate and peroxide. Although no proof of equilibrium can be offered, it is reasonable to assume it was attained.

The material from the above operation was quantitatively diluted to 200 ml. with distilled water giving a zirconium stock solution of 5.7×10^{-3} M. Five milliliter aliquots of this solution were diluted to 25 ml. for the exchange studies.

A preliminary test showed that the resulting solution quantitatively exchanged with the resin and that it was therefore well below the pH limit for appreciable colloid formation. Ammonium hydroxide was added in small increments to raise the pH of successive samples to higher values. Addition of ammonium ion of course sets up a competitive exchange between hydrogen ion and ammonium ion and therefore introduced an unknown into the system. All solutions were therefore made 0.520 M in ammonium chloride, a value large enough to permit ignoring the small amounts from the added base.

C. Experimental Procedure

Twenty milliliter aqueous samples were used for all equilibrations, varying from each other only in hydrogen ion concentration. Twenty-five milliliter volumetric flasks were used for making up the samples; the order of mixing the components was considered important. To 10.00 ml. samples of 1.300 M ammonium chloride 0.15 M ammonium hydroxide was added in amounts varying between samples from 0.5 to 4.5 ml. in 0.5 ml. increments. After the ammonium chloride and ammonium

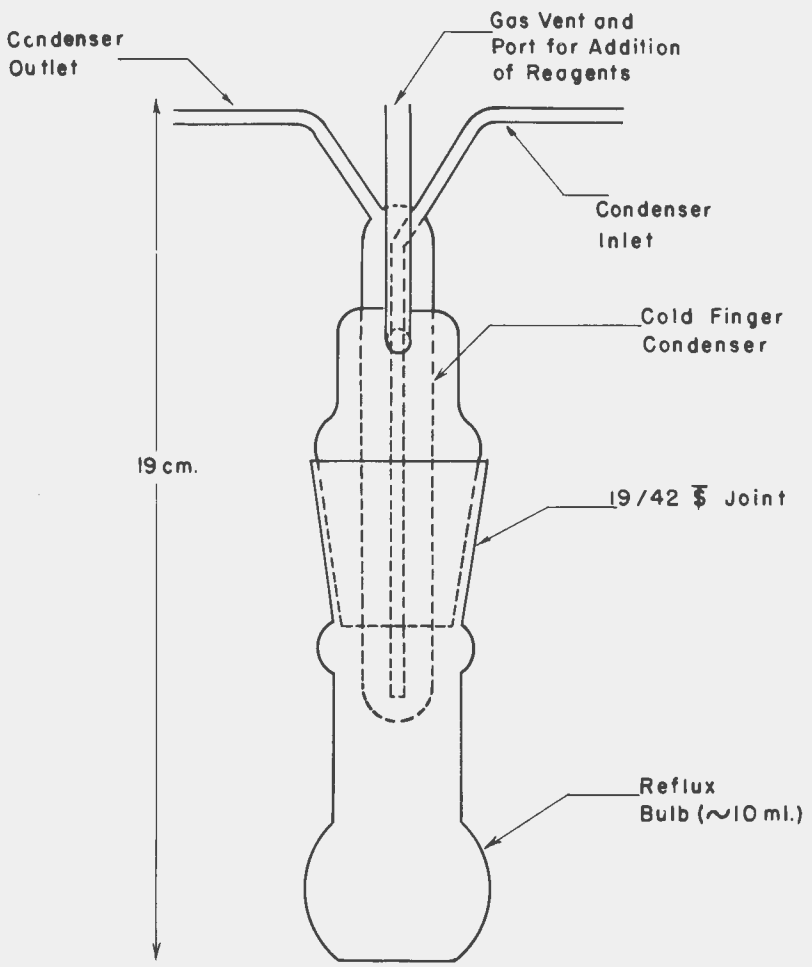


Fig. 3 Semi-Micro Reflux Apparatus for Equilibration of Carrier with Zr^{95}

hydroxide were thoroughly mixed, 5.00 ml. of the active zirconyl chloride previously described were added. The buffering action of the ammonium chloride was used to advantage to prevent the zirconium from being added to too basic a solution giving rise to localized reactions. After dilution to 25.00 ml. the pH of the resulting mixture was measured.

The ammonium concentration of the solutions was sufficiently large and the amount of replaceable hydrogen in the resin great enough that the exchange of ammonium with hydrogen could change the hydrogen ion concentration of the equilibrium mixture by a large factor; each resin sample was therefore pre-equilibrated with 0.520 M ammonium chloride at the measured pH of the active solution to be exchanged with it. With this precaution the pH of the solutions was considered constant over the course of the exchange reaction.

The resin was added to the active sample after it had been thermostatted long enough to establish thermal equilibrium with the water bath. The samples were agitated continuously during the runs with a Burrell shaker set to provide a gentle agitation of the resin. A preliminary run with the system showed that equilibrium was reached within an hour after mixing; however, all solutions were allowed to run in the thermostat under continuous agitation overnight.

After the prolonged equilibration period a small aliquot was removed for counting. This sample was centrifuged for a minute to settle any resin fines produced by abrasion during the equilibration. A 500 μl. sample was then withdrawn and mounted for counting. Plastic counting planchets were used rather than the more conventional metal ones because of the rather high acidity of the solutions. Since the ammonium chloride concentration was constant throughout all the runs, no separation of zirconium from this solid matter was necessary. Mounting the samples in a similar manner produces a constant self-absorption effect that is not observed in the zirconium assay.

Determination of the zirconium was done by a differential counting technique which theoretically obviates the necessity of a separation between zirconium and its niobium daughter activity. The currently accepted decay scheme of the zirconium-niobium pair is shown as Figure 4.[12] It will be observed that the zirconium decays by beta emission to either of two niobium daughters, the 65 day Nb^{95} ground state or its nuclear isomer, Nb^{95m}, a 90 hour gamma emitter which decays to the ground state. The ground state decays by beta emission to Mo^{95} which is stable. Attention is directed to the fact

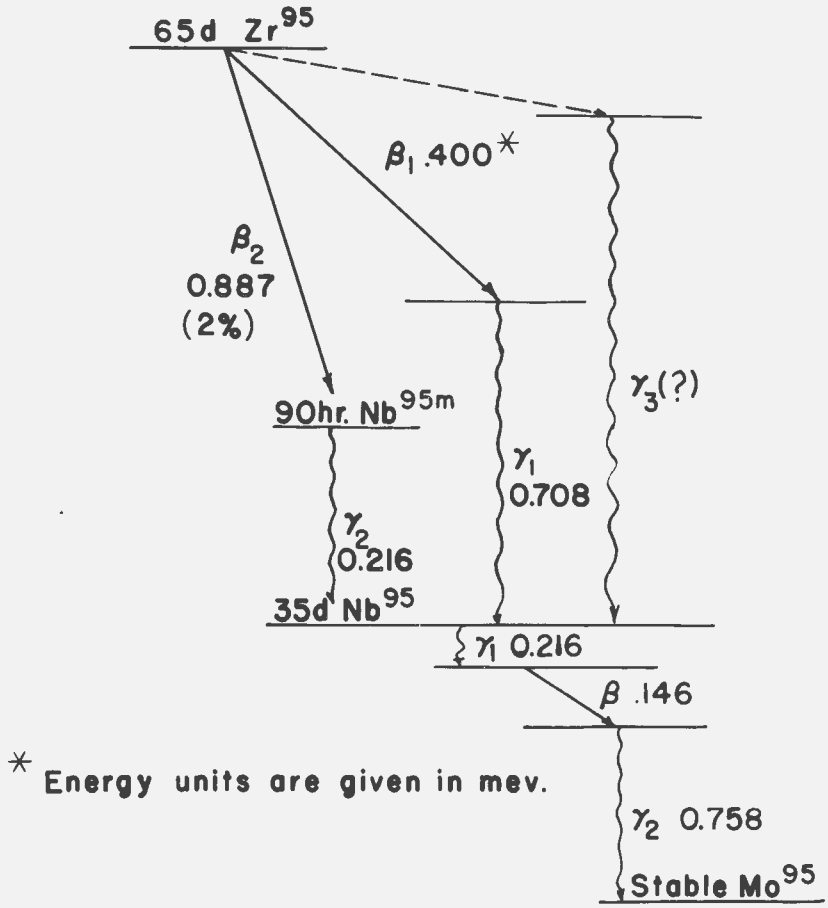


Fig. 4 Decay Scheme of Zr^{95} - Nb^{95}

that the zirconium possesses the more energetic of the two beta radiations. Samples were therefore counted first through a thin aluminum absorber, 28 mg./cm^2, and again through a thick absorber, 454 mg./cm^2. The thin absorber is sufficiently thick to exceed the range of the weak beta rays emitted by Nb^{95}, which were therefore not counted. The only radiations counted were part of the beta rays of the zirconium and the gamma rays from all three nuclides plus the natural background. The heavy absorber was thick enough to absorb all the beta radiation of Zr^{95} but not sufficiently thick to appreciably affect the gamma rays. The difference between the two counting rates was thus the observed zirconium activity. Since the zirconium beta radiations were appreciably absorbed by the thinner aluminum foil, a calibration of the method was made using the same counting technique with a known weight of zirconium as a standard. This standard then gives the apparent specific activity of the zirconium solutions in counts per min. per mg. Zr, and the ratio of the observed counting rate of any sample to this specific activity is the weight of zirconium in that sample.

All counting was done with a Tracerlab end-window Geiger-Meuller tube connected to a scale of 64 electronic scaling unit. The tube was mounted in a Technical Associates lead housing and the samples were counted on "second shelf" geometry.

D. Experimental Results

1. Theoretical Discussion

It has been demonstrated that ion exchange resins are governed by the law of mass action[10] and are subject to thermodynamic treatment. The ion exchange can be characterized by the general chemical equation:

$$\nu AR + B^{+\nu} \longrightarrow BR_{\nu} + \nu A^{+}$$

where A represents any univalent ion, $B^{+\nu}$ any other ion of charge $+\nu$, and R the resin matrix. The thermodynamic equilibrium constant for the reaction is therefore:

$$K = \frac{(a_{BR_\nu})\ (a_{A^+})^\nu}{(a_{AR})^\nu (a_{B^{+\nu}})} \quad . \qquad (1)$$

It is difficult to apply this equation to experimental cases because the activities of the resin compounds indicated are those of the solid phase. If it is assumed that the resin is an ideal solid solution of the two exchanging ions, the activities of the resin components become equal to their mole fractions. Equation (1) thus reduces to

$$K = \frac{(N_{BR_\nu})(C_{A^+})^\nu}{(N_{AR})^\nu (C_{B^{+\nu}})} \times \frac{(\gamma_A)}{(\gamma_{B^{+\nu}})} \qquad (2)$$

where C has been introduced for the aqueous concentrations of the components and γ for their activity coefficients. It should be noted that the activity coefficients thus signified are not generally available since they refer to activity coefficients of each of the repective components in the presence of the other.

If one of the components is present in great excess and is kept at constant concentration some simplifying assumptions can be made. First, the activity coefficient of the minor component it if is present only in trace quatities will remain constant since it is determined largely by the concentration of the major component. Second, the activity of the major component will remain constant since its concentration is constant. This implies that the solution is so concentrated in one of the exchanging ions that the small amounts liberated or adsorbed by reaction with the resin do not appreciably affect its concentration or its activity. Furthermore, if the concentration of this major component is sufficiently high, its mole fraction in the resin will always be approximately unity and K becomes independent of the charge on the ion. With these conditions in mind a pseudo-constant for the exchange reaction can be defined by:

$$k = N_{BR_\nu} / C_{B^{+\nu}} \, . \qquad (3)$$

This quantity is related to the thermodynamic equilibrium constant by:

$$k = K \frac{(N_{AR})^{\nu} (\gamma_{R^{-\nu}})}{(C_{A^{+}})^{\nu} (\gamma_{A^{+}})^{\nu}} . \qquad (4)$$

In the derivation given above only two exchanging ions were considered; however, the zirconium system investigated contains at least three, H^{+}, NH_4^{+}, and one or more zirconium species. The exchange constants for a number of cations have been measured by other workers. If one defines the equilibrium constant given in equation (1) in terms of concentrations rather than activities, the value for the ammonium-hydrogen exchange is found to be 1.18 on Dowex-50.[13] Thus with the very large ammonium chloride concentration in the solutions studied (0.520 M) and the comparatively small hydrogen ion concentration ($\sim 10^{-2}$ M), the resin can be considered entirely in the ammonium form. The exchange is thus observed between ammonium and zirconium ions. The principle function of the varying hydrogen ion concentration is the alteration of the relative amounts of the zirconium species present. Strong variations of k were therefore anticipated as the zirconium assumed a more hydrolytic or polymeric character, indicated by lowering of the k values with decreasing acidity.

2. Experimental Data

The exchange data were not easily reproducible since a time dependency of the extent of exchange was noted. The origin of the irreproducibility is undoubtedly linked with the time dependency of the hydrolysis and polymerization of zirconyl chloride as detected conductometrically. The data show a very strong exchange of zirconium at higher hydrogen ion concentrations. This drops off rapidly as the acidity is decreased and then levels off to a nearly constant value. Little significance is attached to the actual values of the zirconium concentrations reported for the two most acidic solutions since these represent almost quantitative removal of the zirconium. Errors in the counting technique used were appreciable at the low counting rates observed for these solutions, and the actual concentrations could be zero. Beyond these points, however, the counting rates became high enough to make the data reliable. Two series of data are presented, one set obtained by adding the resin to the active solutions immediately after their preparation and the other by adding the resin to the solutions after they had stood

thermostated for periods of up to three days. In all cases the extent of exchange decreased with time as could be seen by marked lowering of the k values. No attempt was made to determine the actual minimal values of k; therefore the observed values represent only upper limits. The exchange data are reported in Table I and the behavior of k with acidity is plotted as Figure 5.

E. Conclusions

It is possible to deduce upper limits for the percentage of the zirconium species which are cationic in the solutions studied. The first sample run shows almost quantitative exchange of the zirconium. In general the relative resin affinities of differing ions are functions of two variables: the ionic charge and the ionic radius. Ions with higher charges are adsorbed many orders of magnitude more strongly than lower charged species, and in all cases investigated by Boyd and his co-workers[10] within any valence group those ions with the larger ionic radii are the more strongly held. The exchange data for zirconium are certainly in accord with these criteria.

The existence of polymers in all the solutions studied must be considered since they were shown to exist[9] in solutions a factor of 100 more acid and a factor of five more dilute than in the present case; however, the complete exchange at the highest acidity studied shows that at least up to a point the polymers as well as all the simple ionic species exchange with the resin. The question of exchange mechanism cannot be resolved with these data. It is conceivable that the polymers undergo de-polymerization before exchanging and it is also possible that small polymers may exchange directly as single ions.

The exchange constant observed is so large that one may assume that all cationic forms are quantitatively exchanged and the zirconium not exchanged is either anionic or colloidal or very highly polymeric. With this assumption the ratio of the total moles adsorbed to the total moles of zirconium available becomes the percentage of exchangeable zirconium in the system. Because of the uncertainty of the behavior of high polymers and because of the time dependency of the exchange, the exchangeable zirconium calculated can be considered only as an upper limit of the cationic content. The data indicated by asterisks in Table I are therefore omitted from this discussion. Table II gives the maximum percentage of cationic zirconium at each of the acidities

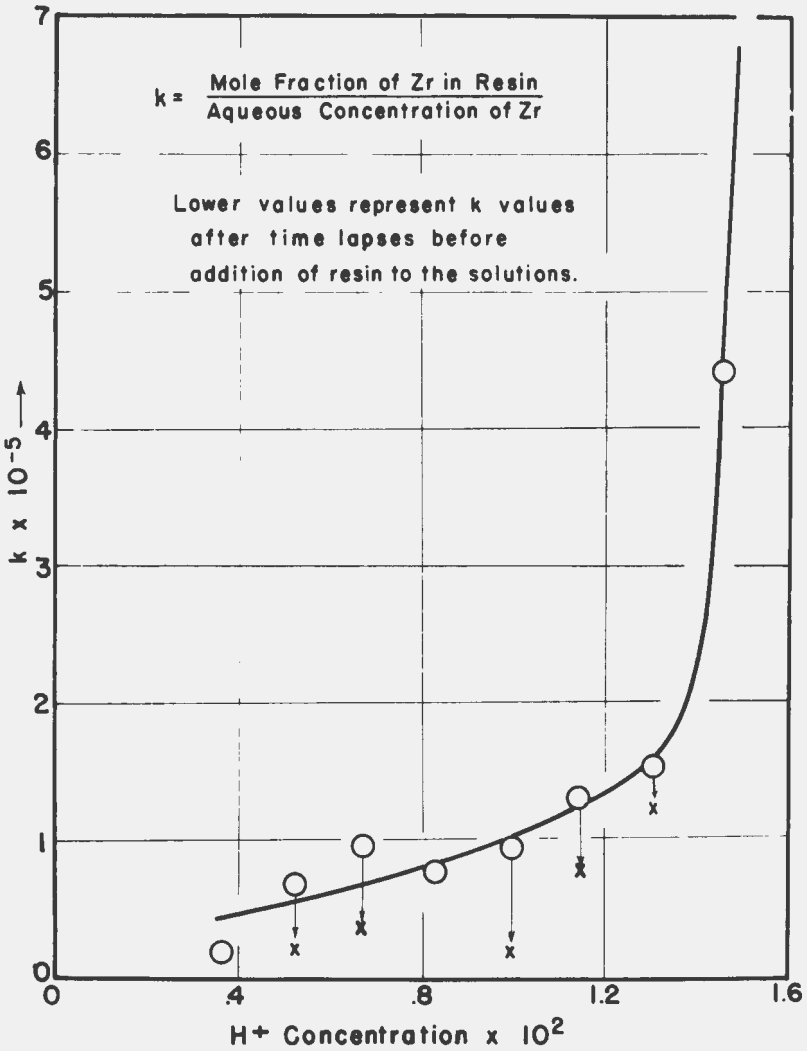


Fig. 5 Behavior of k with Varying Acidity

investigated; the data are presented graphically as Figure 6.

In general it may be concluded that zirconyl chloride at 1.14×10^{-4} M is largely ionic in nature but is seen to undergo marked changes in the neighborhood of pH 2. At this acid strength it changes rapidly to a highly complicated system involving probably both complex ions and colloid formation as the acidity is decreased. The change in its character is shown to be time dependent.

V. PART II. THE SLOW HYDROLYSIS OF ZIRCONYL CHLORIDE

A. General Procedure

In part one the ion exchange properties of zirconyl chloride were studied in order to determine the extent of polymerization and hydrolysis of the material in very dilute solution; in connection with this study a time dependency of the results was observed. Further investigation of the same system by means of conductivity measurements was considered advisable in order to determine the actual time dependence of the hydrolysis. The acidity of the solutions was measured initially and at the end of the experiment. Data was taken at 25° C. and at 35° C.

B. Preparation of Materials and Apparatus

1. Zirconyl Chloride

Zirconyl chloride was prepared by recrystallization from concentrated hydrochloric acid, the standard method of procedure. The same material used in part one was used here again as a raw material. The crystals were air-dried overnight, and then put into solution in a small volume of water. This solution was allowed to stand three days and was then used as a stock solution for dilution to the samples which were measured. Because of the uncertainty of the presence of excess acid trapped within the crystals, the stock solution was analyzed for zirconium gravimetrically and for chloride by the Mohr method. The formula $ZrOCl_2$ was assumed to be the formula of the compound and the excess chloride content observed was assumed to be free hydrochloric acid.

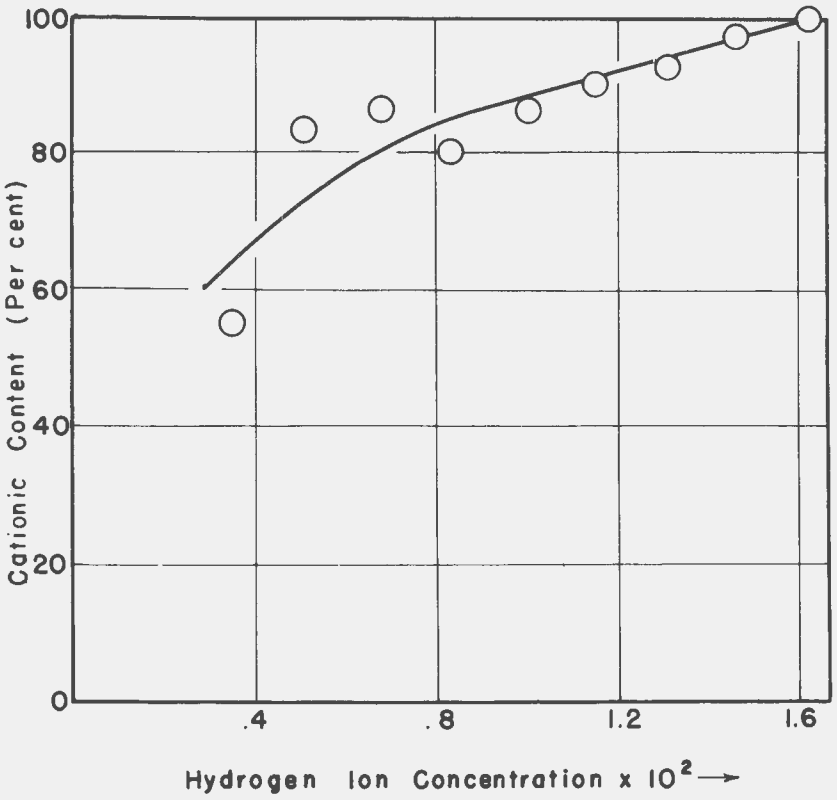


Fig. 6 Maximum Cationic Content of 1.14×10^{-3} M $ZrOCl_2$ at Various Acidities

Table II

Maximum Cationic Content of Zirconyl Chloride Solutions

Sample	(C_{H^+}) M/l. x 10^2	Total Moles Initial	Zr At Eq.	Total Moles Exchanged	Per Cent Cationic
1	1.62	228×10^{-7}	$.46 \times 10^{-7}$	227×10^{-7}	100
2	1.46	"	6.0 "	222 "	97
4	1.31	"	23.4 "	210 "	92
6	1.15	"	29.0 "	205 "	90
8	1.00	"	32.6 "	195 "	86
9	.831	"	44.6 "	183 "	80
11	.675	"	34.8 "	195 "	86
13	.515	"	39.7 "	188 "	83
14	.355	"	102 "	126 "	85

Table I

Exchange Data for Zirconium-Ammonium Ions on Nalcity HCR

Sample	Resin Weight, meq.	$(H^+) \times 10^2$ moles/l.	Zr Concentration $\times 10^6$ moles/l. Initial	Zr Concentration $\times 10^6$ moles/l. At Eq.	Moles Zr Adsorbed $\times 10^5$	N_{ZrR} x 10	k x 10^{-5}
1	22.9	1.62	1140	2.3	2.27	16.0	43
2	16.7	1.46	1140	30.2	2.22	19.0	4.4
3	18.0*	1.31	1140	96.4	2.10	15.3	1.21
4	11.5	1.31	1140	117	2.05	17.8	1.52
5	13.5*	1.15	1140	188	1.91	14.1	0.78
6	10.6	1.15	1140	145	1.99	18.9	1.30
7	14.2*	1.00	1140	545	1.19	8.5	0.16
8	13.0	1.00	1140	163	1.95	15.0	0.92
9	10.7	.831	1140	226	1.83	14.2	0.76
10	15.6*	.675	1140	296	1.68	10.8	0.36
11	11.8	.675	1140	174	1.95	16.5	0.95
12	13.4*	.515	1140	426	1.44	10.7	0.25
13	14.0	.515	1140	199	1.88	13.4	0.67
14	12.6	.355	1140	511	1.26	10.0	0.19

*Indicates points run after long standing.

2. Conductivity Apparatus

The conductivities were measured with a simple resistance bridge. Its circuit diagram is given as Figure 7.

It is extremely important in such measurements that the signal put out by the oscillator be a pure sine wave. Over a long interval any slight direct current component will produce electrode reactions that can alter the conductivity. The oscillator used was a Hewlett-Packard, Model 202D which has less than two percent distortion at ten volts, its maximum output. The frequency used for the determinations was varied getween 400 and 1500 cycles and in general was kept as low as possible to minimize inductive and capacitative effects in the system.

C. Experimental Procedure

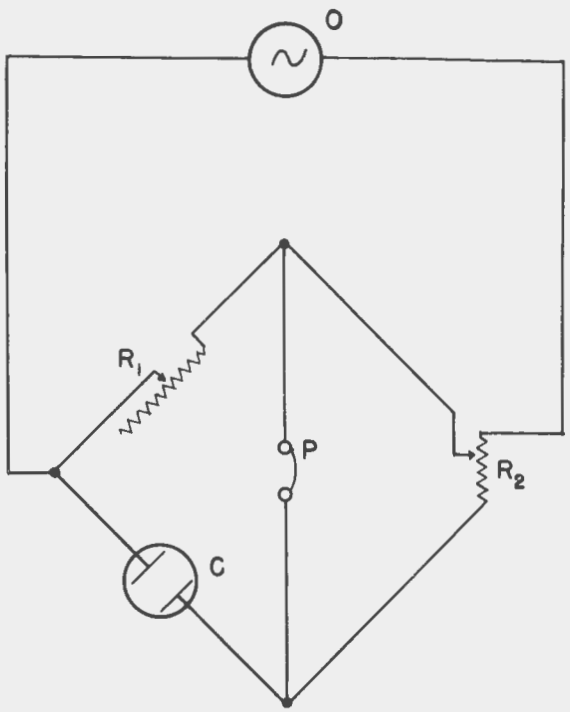
The conductivity cells and the water used for dilution were thmostatted prior to the run. The first points were taken within five minutes of the time of mixing. The resistance of the cell was actually measured by adjusting the slide wire to its midpoint and obtaining the null point with the decade resistor shown in the diagram. The first few null points were checked with an oscilloscope but its use was discontinued after the earphones proved equally suitable.

D. Experimental Results

The conductivity was observed to increase rapidly for the first few hours in both experiments, then to increase more slowly for many hours longer. A stable value was not observed in either experiment. The curves for conductivity versus time are shown as Figures 8a and 8b.

The hydrogen ion content of the system was measured twice during the runs, initially and at the time of the final conductivity measurement. It was impossible to get the initial hydrogen ion concentration by a direct measurement since the system undergoes appreciable change in a very few minutes; the initial value was therefore obtained by measuring the acidity of the stock solution and calculating the value on dilution to the concentration used. The final value was of course measured directly since the system no longer changed appreciably in a few minutes interval.

The analytical results are given in Table III.



R_1 - Decade Resistance
R_2 - 25 ~ Potentiometer
C - Conductivity Cell
P - Crystal Headphones
O - Audio-Frequency Oscillator

Fig. 7 Circuit Diagram of Conductivity Bridge

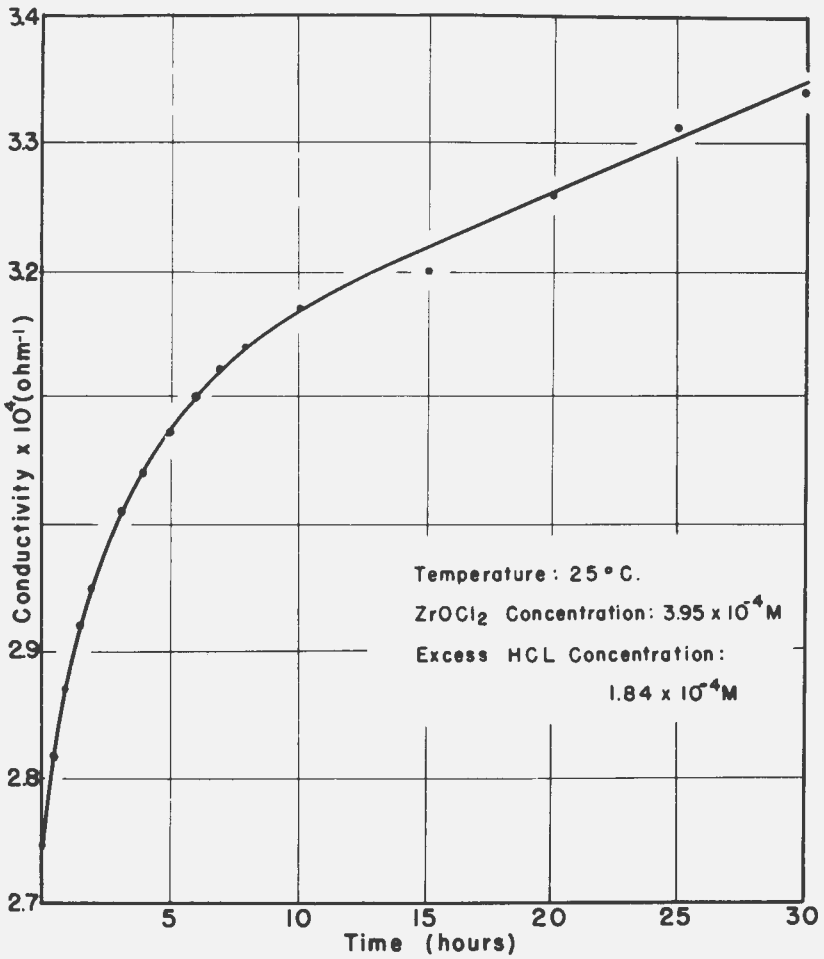


Fig. 8a Variation of Conductivity of $ZrOCl_2$ with Time

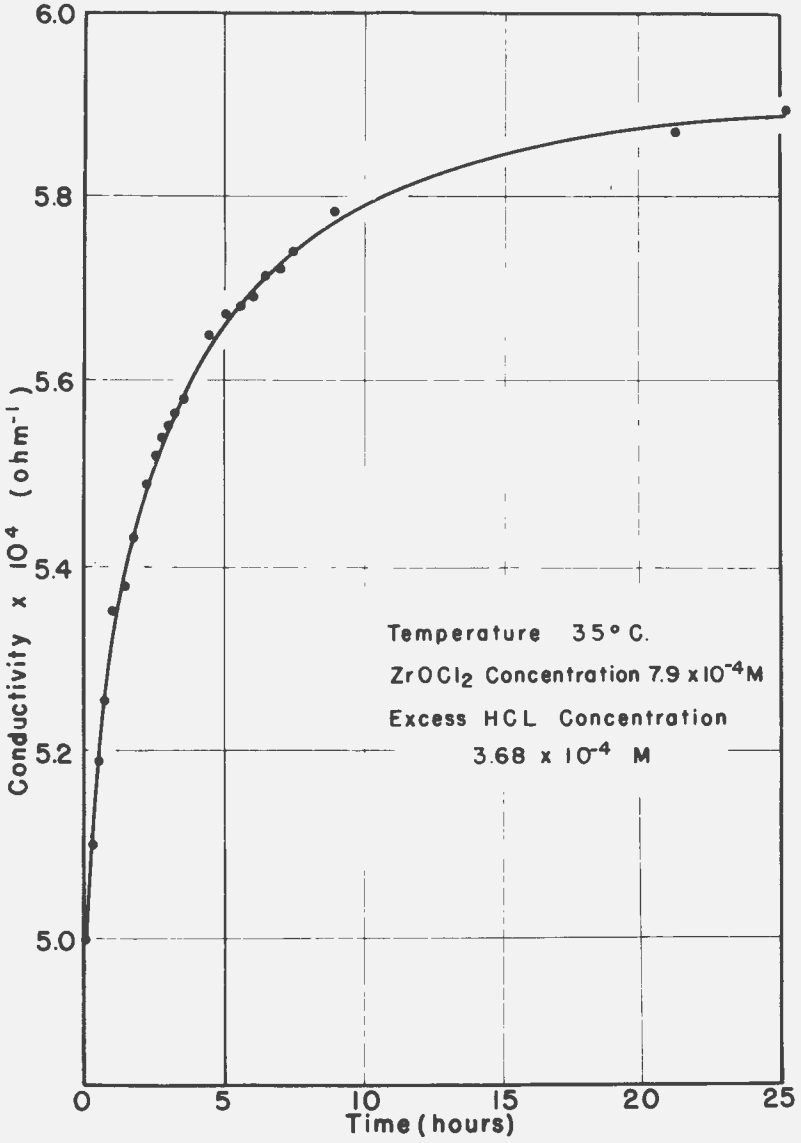


Fig. 8b Variation of Conductivity of $ZrOCl_2$ with Time

Table III

Composition of Zirconyl Chloride Solutions

		Sample 1 25°	Sample 2 35°
Zirconium Content	(moles/l.)	3.95×10^{-4}	7.90×10^{-4}
Chloride Content	(moles/l.)	9.74×10^{-4}	19.48×10^{-4}
Chloride (HCl) Excess	(moles/l.)	1.84×10^{-4}	3.68×10^{-4}
Hydrogen Ion Content			
Initially	(moles/l.)	2.5×10^{-4}	5.25×10^{-4}
Finally	(moles/l.)	5.0×10^{-4}	8.32×10^{-4}

It can be seen that even initially the hydrogen ion concentration is greater than the chloride ion excess; the excess hydrogen ion is produced by the hydrolysis of the zirconium compounds in solution.

E. Conclusions

The specific conductivity of any solution, designated traditionally as L, is obtained by dividing its measured resistance by the cell constant. This specific conductivity is the sum of the specific conductivities of all the species present. In solutions of strong electrolytes which are sufficiently dilute the specific conductivity of any species divided by 10^3 M where M is the molarity of the ion is very nearly the equivalent conductance, λ, of the ion at infinite dilution multiplied by its charge. With a knowledge of the concentrations and equivalent conductances of all the ionic species but the zirconium one may assign an apparent conductance to the zirconium ions. The work of Connick and McVey[8] indicates that zirconium is little complexed by chloride ion in strong acids; however, little is known about the situation in very dilute acid. For the purpose of this

investigation it was assumed that the chloride ion was independent of the zirconium and was not bound with it to any very large degree. Because of the very high chloride dilution this is a reasonable assumption. To find the zirconium conductivity one need only solve the equation:

$$10^3 L = \Lambda_{H^+}(C_{H^+}) + \Lambda_{Cl^-}(C_{Cl^-}) + \sum_{i=1}^{j} \Lambda_i (C_{Zr_i}) \quad (1)$$

where j is the maximum number of kinds of zirconium ions in solution. One may do little but guess at the value of j.

Since two independent properties, the conductivity and the acidity, were measured, one may assume values for j of one and two and solve simultaneous equations for the conductivities of the ions assumed. The data at either temperature may be used for the calculations and the data at the other temperature may be used as a check. The thermal coefficient of conductance of nearly all ions is of the order of .02/°C., very near the thermal coefficient of viscosity of water. It is reasonable to expect that the correctly assigned conductances of zirconium species will reflect this nearly uniform constant.

A large variety of ions were assumed and the calculations based on these assumptions were tested for this property. No consistency was observed and in most cases the temperature coefficient derived was not even in the right direction. The simplest assumption one may make in regard to the hydrolysis of zirconyl chloride is that it undergoes the following reaction:

$$ZrO^{++} + H_2O \rightleftharpoons ZrOOH^{+} + H^{+}$$

The two ions ZrO^{++} and $ZrOOH^{+}$ are therefore the conducting species. With the assumed stoichiometry the concentration of ZrO^{++} at any time is equal to the total zirconium content less the hydrogen ion derived from the hydrolysis reaction, and the concentration of $ZrOOH^{+}$ is equal to the concentration of hydrolytically produced hydrogen ion. The hydrogen ion produced by hydrolysis can be found by subtracting the chloride ion excess from the measured concentration of hydrogen ion. Equation (1) therefore becomes

$$10^3 L = \Lambda_{H^+} \times C_{H^+} + \Lambda_{Cl^-} + \Lambda_{ZrOOH^+} C_{ZrOOH^+}$$

$$+ \Lambda_{ZrO^{++}} \times C_{ZrO^{++}} \qquad (2)$$

or,

$$10^3 L = \Lambda_{H^+} \times C_{H^+_t} + \Lambda_{Cl^-} \times C_{Cl^-_t} + \Lambda_{ZrOOH^+}(C_{H^+_{hyd}})$$

$$+ \Lambda_{ZrO^{++}}(C_{Zr_t} - C_{H^+_{hyd}}) \qquad (3)$$

where t has been introduced as a subscript to indicate the total concentration of the given ion and H^+_{hyd} to indicate the hydrogen ion liberated as a product of the hydrolysis. All concentration data necessary for substitution into this equation are available in Table IV. The accepted values of Λ_{H^+} and Λ_{Cl^-} at 25° are 348 and 76.3, respectively. Their thermal coefficients of conductivity are .014 and .019 per degree respectively. With substitution of the experimental values two equations representing initial and final conditions are obtained at each temperature. There are two unknowns, namely, the conductances of the two zirconium species; they may be found by simultaneous solution of the two equations. The values obtained for these conductances are listed in Table Iv.

The derived values of equivalent conductances for zirconium though reasonable at 35° C. are higher than one would expect for the assumed ions by a factor of about two at 25° C.; the temperature coefficient is negative. The reason for this discrepancy must lie in the stoichiometry assumed for the hydrolysis. The concentrations of hydrogen and chloride ions are known; therefore, the error must lie in the number or type of zirconium species chosen for the calculation. Since essentially the same results are obtained if only one conducting species is assumed, it appears that the solution contains some very highly conducting species. The highly conducting species cannot be assigned to polymeric ions of high charge since the zirconium concentration would be decreased by a factor commensurate with the number of zirconium atoms in the average polymer, leading to values of conductivity much too high to be reasonable. Furthermore,

Table IV

Specific Ionic Conductances of Aqueous Zirconyl Chloride

	25°C.	35°C.
a. Total Specific Conductance, L		
initially	2.74×10^{-4}	5.00×10^{-4}
finally	3.34×10^{-4}	5.89×10^{-4}
b. Chloride Specific Conductance ($\Lambda_{Cl^-} \times C_{Cl^-} \times 10^{-3}$)		
initially	$.743 \times 10^{-4}$	1.765×10^{-4}
finally	$.743 \times 10^{-4}$	1.765×10^{-4}
c. Hydrogen Ion Specific Conductance ($\Lambda_{H^+} \times C_{H^+} \times 10^{-3}$)		
initially	$.875 \times 10^{-4}$	2.090×10^{-4}
finally	1.750×10^{-4}	3.270×10^{-4}
d. Zirconium Specific Conductance $[a-(b+c)]$		
initially	1.232×10^{-4}	1.145×10^{-4}
finally	$.847 \times 10^{-4}$	$.852 \times 10^{-4}$
e. ZrO^{++} Equivalent Conductance, derived		
($\Lambda_{ZrO^{++}}/2$)	156	84
f. $ZrOOH^+$ Equivalent Conductance, derived		
($\Lambda_{ZrOOH^+}/1$)	227	52.4

the total current carrying capacity of polymeric ions could not be very large because of the decreased mobility. Neither can the discrepancy lie in the complexing of the zirconium with chloride since attachment of chloride to zirconium would decrease the chloride content of the solution and again give unreasonably high conductivities. It is possible that the hydrolysis of zirconyl chloride can proceed in the direction of more highly charged zirconium monomers such as Zr^{+4} and $ZrOH^{+3}$ as well as toward the lower charged species $ZrOOH^{+}$; this does not appear likely in consideration of the known chemistry of zirconium. It should be noted that the very high conductivity assignable to zirconium from this experiment qualitatively confirms the data of Pauli and Adolf[5] who observed this same phenomenon.

VI. DISCUSSION

The slow hydrolysis of zirconyl chloride has been observed by two different methods, ion exchange and conductivity. From the data obtained the rate-determining step could not be identified. It would appear that further investigation of the ion exchange properties of zirconium would provide vital information on its aqueous properties. Upper limits of the cationic content of 1.14×10^{-3} M zirconyl chloride have been set by ion exchange measurements. Further investigation of aged solutions should demonstrate whether zirconyl chloride actually reaches an equilibrium in its hydrolysis.

The time dependency of conductivity of zirconyl chloride has been observed conductimetrically. The conductivity of the zirconium species present is higher than one would expect and cannot be explained in terms of any of the assumptions made. Pauli and Adolf[5] came to the conclusion that zirconium can exist as anions as well as cations and explained their conductivity and freezing point data in terms of anions. Their data apparently has not been checked and their conclusions were based on assumptions no longer considered valid. However, the possible existance of anions cannot be completely discounted. Although anion exchange resins are not as well understood as their cation counterparts, studies with these materials could decide whether anionic forms actually exist.

Additional data on the time dependency of the zirconium conductivity would also be of value. The data taken by Ruer and by Venable and Jackson cannot be accepted today because

of the lack of control of the signal put into their systems. Modern electronic audio-oscillators are capable of almost pure sine wave output; their data should be checked with these instruments. More accurate data on this reaction will undoubtedly lead to the discovery of the rate controlling step and a complete mechanism for the reaction. The data herein observed by conductivity measurements have indicated the existance of three or more conducting species in 10^{-4} M $ZrOCl_2$.

The errors in the above experiments while not large should be enumerated.

(1) The determinations of zirconium weights in the samples counted were done by radiation assay and depend upon the reproducibility with which one can mount two successive samples of the solutions. In general this is considered to be about five percent. This is the largest single source of error in the experiments and all others were relatively small in comparison with it.

(2) The weights for the resin samples were taken to be constant when the weights were reproducible within .5 mg. after several hours drying. This could possibly produce an error of one part in two hundred or .5 percent, well within the limit imposed by the reproducibility of mounting.

(3) The disintegrations of radioactive emitters can be treated by the methods of statistics and the probably error in any one observation calculated. Very long counts were taken of all samples because the zirconium counts are represented as the difference between two relatively large numbers. Count lengths were so regulated that the probable error in the difference became less than two per cent of the observed value, again within the limit imposed by the reproducibility. The methods of adjusting this time are adequately treated in textbooks on nuclear phenomena.[14,15]

(4) Zirconyl chloride was treated in accordance with established practice as a true compound for the purposes of calculating the apparent ionic conductances mentioned in the conductance experiments; however, it will be observed that the analytical chloride content was almost exactly three times the zirconium content. It was assumed that the extra chloride was due to free hydrochloric acid trapped within the crystals as they were formed in the purification process. Other workers have reported the isolation of solid zirconium chlorides in which the ratio of chloride

was less than the stoichiometric two for $ZrOCl_2$; these were prepared in relatively dilute acid. One may thus question whether zirconyl chloride is a compound which can be isolated over wide ranges of acid and zirconium from solution or whether a whole series of compounds representing various degrees of hydrolysis of the zirconium may be formed. A thorough study along the lines of the phase rule for the system ZrO_2, HCl, H_2O has apparently never been carried out. Such a study would be of appreciable value in zirconium chemistry.

VII. SUMMARY

The ion exchange properties of zirconyl chloride have been studied in solutions 1.4×10^{-3} M in zirconium and .52 M in ammonium chloride; the cationic content of the solutions was found to vary from 99 per cent to about 55 per cent as upper limits in the acid range 1.62×10^{-2} M to 3.55×10^{-3} M.

A time dependency of the exchange of zirconium was noted and in an attempt to discover its nature conductance measurements at 10^{-4} M zirconium were made as time studies. Conductance curves were run at 25° and 35° C.; unfortunately they were not subject to analysis in terms of the probable species present. At least three conducting species were present in the solutions and the measurements permitted the simultaneous observation of only two. The measurements are believed to be among the most accurate so far reported and the concentrations investigated were much below the previous reports.

Further studies along the lines of this investigation have been outlined for obtaining additional information on the aqueous behavior of zirconyl chloride.

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